

A Density Functional study of Covalency in the Trihalides of Lutetium and Lawrencium

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Abstract

In this work we present a four component relativistic theoretical investigation of the trihalides of lutetium and lawrencium, LuX_3 , LrX_3 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) respectively using density functional theory (DFT) with different density functional and a geometrical optimisation procedure as implemented in DIRAC-package. The results show the trend of bonding from lighter to the heavier halide atoms and between 4f/5f atoms Lu and Lr.

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I. INTRODUCTION

In a 1988 review in the *Handbook on the Physics and Chemistry of Rare Earths* C. K. Jørgensen asked the rhetorical question 'Is Quantum Chemistry feasible ?' and with special regard to these elements he answered 'Sorry, not today; perhaps next century' [1]. Presently, in the new century, the structure and reactivity of f elements is a flourishing domain of theoretical chemistry [INSERT reviews..] The main features of the chemistry of the lanthanides and the actinides can be deduced from simple atomic calculations. In Figs. 1-4 we present orbital properties extracted from numerical 4-component relativistic Hartree-Fock calculations[2] averaging over the valence configuration $(n-2)f^x(n-1)d^1ns^2$, ($x = 1, 14$) for the neutral lanthanide and actinide atoms. We have chosen this configuration, which is not the ground state configuration for all the f elements, since it gives access to information about the $(n-2)f$, $(n-1)d$ and ns orbitals. From the orbital energies in Fig. 1 we observe a distinct energetical separation of the $4f$ orbitals from the $5d$ and $6s$ orbitals of the lanthanides which explains their chemistry dominated by the +3 oxidation state. We note that the $5d$ levels cross the $6s$ level towards the end of the series, a feature which may induce convergence problems in atomic calculations not exploiting the full atomic symmetry. Fig. 2 shows a somewhat different situation for the actinides in that the $5f$ levels are energetically close to the $6d$ and $7s$ levels at the beginning of the series, but are then strongly stabilized towards the end of the series. These features translate into a rich oxidation chemistry for the early actinides and a restriction to the +3 oxidation state for the late actinides. This in turn explains the challenge of separating the minor actinides americium and curium from the lanthanides in the treatment of nuclear waste [REF]. Looking at mean radii $\langle r \rangle$, we observe in Fig. 3 a distinct spatial separation of the $4f$, $5d$ and $6s$ orbitals in the lanthanides, whereas the $(n-1)d$ and ns orbitals come quite a bit closer in the actinides. [DISCUSS lanthanide contraction] It is also interesting to observe that whereas the spin-orbit splitting in the $(n-2)f$ shell is considerably stronger than for the $(n-1)d$ shell, any difference in spatial extent is hardly visible for the spin-orbit components of the $(n-2)f$ shell. This can be understood from the fact that the $(n-2)f$ orbitals are in general quite contracted and so any deformation of the orbitals is energetically very much more expensive than for the $(n-1)d$ shell.

With these observations in mind it was all the more surprising when Clavaguéra *et al.* [3] reported a clear example of $4f$ participation in bonding in LuF_3 since lutetium is at the very end of lanthanide series where one would expect the $4f$ orbitals to be the most inert. The conclusion was seriously questioned by Roos *et al.* [4] as well as Ramakrishnan *et al.* [5].

The purpose of the present paper is to investigate the possible $4f$ participation in LuF_3 by an independent

approach. We employ a trick that may be useful for other purposes as well. We extend our electronic structure analysis to all trihalides ($X=F, Cl, Br, I$) of lutetium as well as of lawrencium. We thereby provide a comparison of covalency between these two elements, of relevance for the delicate problem of separation of the late actinides from the lanthanides. The paper is organized as follows: In section II we describe our methodological approach. Computational details are given in section III. In section IV we present and discuss the results of our geometry optimizations and electronic structure analysis, before concluding in section IV B.

II. THEORETICAL CONSIDERATIONS

The question about the participation of $(n-2)f$ orbitals in bonding in the lanthanides and actinides is very much a leading question:

1. It assumes that one can identify these atomic orbitals in the electronic structure of the molecule.
2. It assumes that one can unambiguously distinguish bonding from non-bonding contributions to the electronic structure of the molecule.

In order to tackle the first point we perform 4-component relativistic Hartree-Fock (HF) and Kohn-Sham (KS) calculations of the trihalides of lutetium and lawrencium (LuX_3 and LrX_3 , $X=F, Cl, Br$ and I) and investigate their electronic structure by projection analysis[6], that is we expand the molecular orbitals (MOs) in pre-calculated orbitals (index j) of the constituent atoms (index A).

$$\psi_i^{MO} = \sum_{Aj} \psi_j^A c_{ji}^A + \psi_i^{pol}. \quad (1)$$

The fragment orbitals are usually restricted to the occupied orbitals of the selected configurations of the constituent atoms of the molecule. The expansion is completed by the polarization contribution ψ_i^{pol} which by construction is orthogonal to the fragment orbitals. Once the expansion coefficients c_{ji}^A have been obtained a population analysis may be carried out completely analogous to, but without the basis set sensitivity of a Mulliken population analysis. The selection of fragment orbitals should be adjusted if the gross population of the polarization contribution is significant.

The next point is somewhat more difficult due to the invariance of the electronic energy under rotations of the occupied orbitals of these closed-shell molecules. This rotational freedom can be exploited to transform from canonical Hartree-Fock or Kohn-Sham orbitals to localized orbitals, or, in the terminology of Mulliken[7], from spectroscopic to chemical MOs. However, there is an abundance of possible localization

criteria and thus perhaps not a clear answer from such an approach. The problem would have been simpler for the trihalide of any other lanthanide than lutetium since one would then expect inert $4f$ orbitals to form an open shell. There would accordingly be a *variance* of the electronic energy with respect to rotations between the open- and closed-shell orbitals. However, this immediately suggests the strategy that we will pursue in this paper: We will place $4f$ orbitals from an atomic calculation in an artificial open-shell with fractional occupation close to, but not equal to 14. If the $(n - 2)f$ atomic orbitals now localize to the open shell, we have unambiguous evidence that they are chemically inert.

III. COMPUTATIONAL DETAILS

All calculations reported in this paper are based on the 4-component Dirac-Coulomb Hamiltonian with a Gaussian charge distribution as the nuclear model using the recommended values of Ref. [8]. The numerical atomic calculations were performed using the GRASP code [2]. Molecular relativistic 4-component Hartree-Fock and density functional (PBE [9, 10] and B3LYP [11–13]) calculations were carried out using the DIRAC08 package [14]. We employed the cc-pVTZ Gaussian basis sets of Dunning and co-workers [15–17] for F, Cl and Br and equivalent sets of Dyal and co-workers [18–20] for I, Lu and Lr. The small component basis set for the 4-component relativistic calculations has been generated using restricted kinetic balance imposed in the canonical orthonormalization step[21]. All basis sets are used in uncontracted form. HF and KS geometry optimizations were carried out using analytic and numerical gradients, respectively. For pyramidal (C_{3v}) and planar (D_{3h}) structures we employed the lower C_s and C_{2v} symmetries, respectively. Test calculations with cc-pVDZ basis sets indicate that the reported structures can be considered converged with respect to the chosen basis sets. For the projection analysis fragment orbitals were generated by average-of-configuration HF calculations and KS calculations with fractional occupation, corresponding to ground state electronic configurations of the atoms.

IV. RESULTS AND DISCUSSION

A. Molecular structure

In table I, II we present HF, B3LYP and PBE calculation for lutetium and lawrencium trihalides LuX_3 , LrX_3 ($\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}$) respectively. For the former trihalides, the LuX_3 , there exist a large number of theoretical works whereas very limited works concerned the lawrencium trihalides. Since we will discuss the

two table separately. In table I we summarise our result together with theoretical and experimental values from the literature, given also in the table the method (or the Hamiltonian) and the basis set used to obtain these values. First of all looking to the bond lengths in table I one sees that our values using B3LYP have the best agreement with experimental ones and second there is a good agreement with the literature for the respective method (or Hamiltonian), especially with the HF values of ref. [22],[23] and the PBE of ref. [3]. Concerning the geometrical shape and the bond angle we see that HF give a planar geometry for all the trihalides whereas B3LYP and PBE give a pyramidal geometry for the LuF_3 only and a planar geometry for the other trihalides. Increasing of the bond angle towards the heavier trihalides can be understood having in mind that the heavier halides have weaker ability to polarize the metal atom which means less distribution of the electronic density around the metal atom favoring a planar geometry with the highest bond angle of 120 grad and longer bond length towards the heavier halides as seen in table I.

B. $4f$ orbital participation in bonding in LuF_3

We have studied the possible $4f$ orbital participation in bonding in LuF_3 by the approach presented in sections II and III. The results are summarized in table III. We first calculated the neutral lutetium atom in D_{2h} with linear supersymmetry. The resulting coefficients were exported to C_1 symmetry. The Lu $4f$ orbitals were next imported into a molecular calculation on LuF_3 in the optimized pyramidal geometry and kept frozen in an initial calculation on the neutral molecule. Starting from the resulting molecular coefficients a series of KS calculations with fractional occupation, that is $14-\delta$ electrons ($\delta \in [0.0, 0.2]$) in 14 spinors, were carried out and the resulting molecular orbitals studied by projection analysis. In each calculation vector for each occupied orbital was selected based on overlap with the starting molecular coefficients. However, it is seen from table III that the electronic energy goes smoothly into the energy of the fully relaxed neutral molecule as the hole δ tends towards zero, indicated that we indeed obtained the ground state of the molecule for each value of δ .

Conclusions The presented four component relativistic result for the trihalides of lutetium and lawrencium, LuX_3 , LrX_3 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) respectively using density functional theory (DFT) shows that the trend of bonding is from lighter to the heavier halide atoms and between $4f/5f$ atoms Lu and Lr.

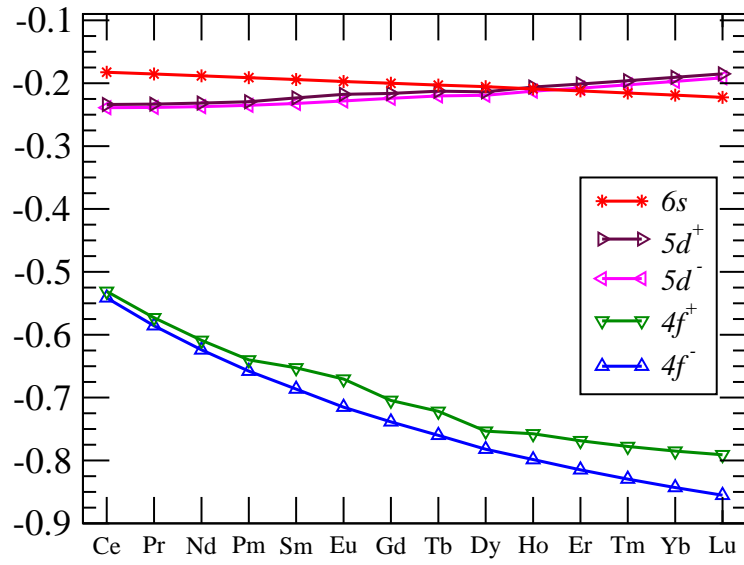


Figure 1. Energies (in a.u.) of the $4f$, $5d$ and $6s$ orbitals for Ce-Lu from 4-component relativistic Hartree-Fock calculations averaging over the $4f^x 5d^1 6s^2$ ($x=1, 14$) valence configuration.

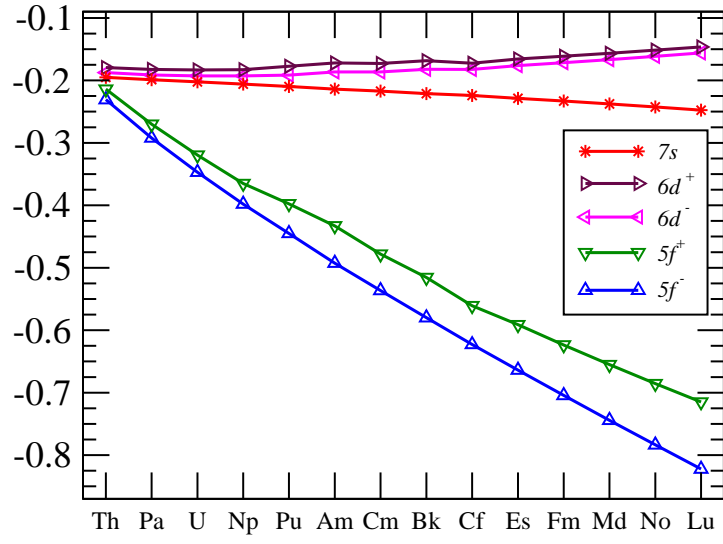


Figure 2. Energies (in a.u.) of the $5f$, $6d$ and $7s$ orbitals for Th-Lr from 4-component relativistic Hartree-Fock calculations averaging over the $5f^x 6d^1 7s^2$ ($x=1, 14$) valence configuration.

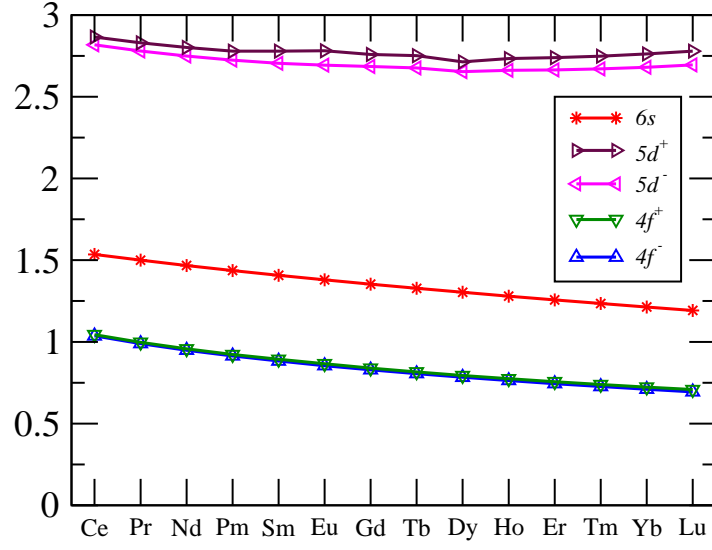


Figure 3. Mean radius $\langle r \rangle$ (in Bohr) of the 4f, 5d and 6s orbitals for Ce-Lu from 4-component relativistic Hartree-Fock calculations averaging over the $4f^x 5d^1 6s^2$ ($x=1, 14$) valence configuration.

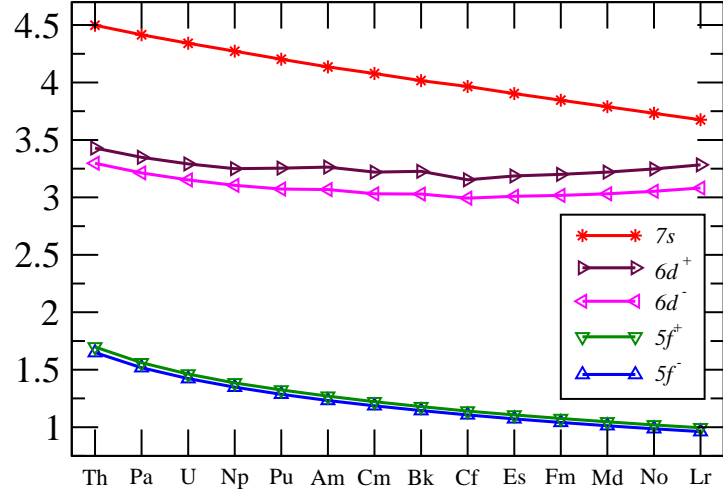


Figure 4. Mean radius $\langle r \rangle$ (in Bohr) of the $5f$, $6d$ and $7s$ orbitals for Th-Lr from 4-component relativistic Hartree-Fock calculations averaging over the $5f^x 6d^1 7s^2$, ($x=1, 14$) valence configuration.

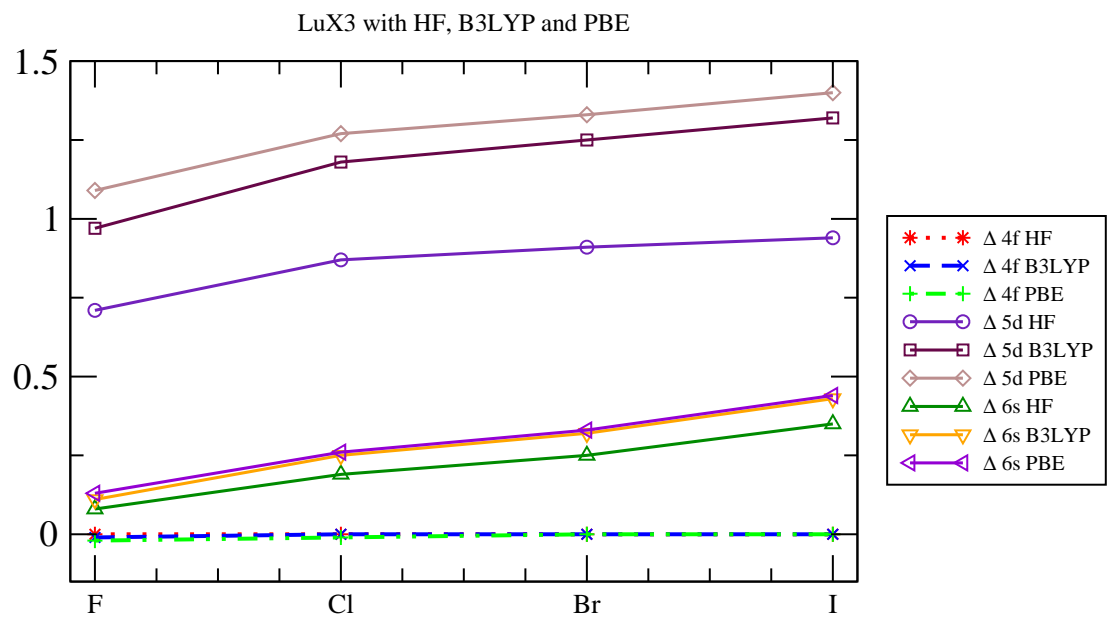


Figure 5. LuX₃ using HF,B3LYP- and PBE- functional, change of population with respect to $4f^{14} 5d^0 6s^0$ configuration

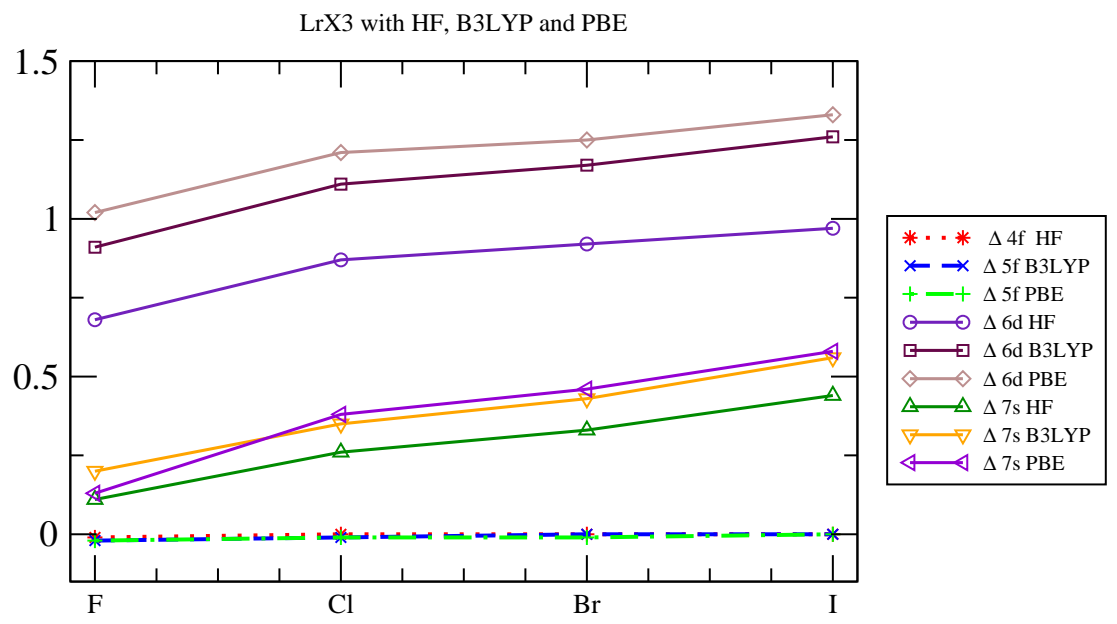


Figure 6. LrX_3 using HF, B3LYP- and PBE- functional, change of population with respect to $5f^{14} 6d^0 7s^0$ configuration

Table I. Geometric parameters of lutetium trihalides LuX₃

Method	Hamiltonian	Basis	Ref	Lu-X bond length (in Å)			X-Lu-X bond angle (in °)				
				LuF ₃	LuCl ₃	LuBr ₃	LuI ₃	LuF ₃	LuCl ₃	LuBr ₃	LuI ₃
HF	DC	cc-pVTZ	pw	1.980	2.440	2.592	2.821	120	120	120	120
HF	RECP	(TZ2D)	[22]	1.984	2.439	–	–	–	–	–	–
HF	RECP/LPP		[23]	1.984	–	–	–	120	–	–	–
B3LYP	DC	cc-pVTZ	pw	1.972	2.407	2.557	2.777	118	120	120	120
B3LYP	RECP	[24]+pol	[25]	1.991	2.447	2.590	2.809	118.9	120	120	120
B3LYP	DKH	ANO-RCC	[4]	1.985	–	–	–	120	–	–	–
B3LYP	RECP		[26]	1.97	2.44	–	–	118.4	119.9	–	–
PBE	DC	cc-pVTZ	pw	1.965	2.393	2.543	2.761	115.6	120	120	120
PBE	ZORA	(QZ4P)	[3]	1.969	2.396	2.544	2.779	116.2 ^P	120	120	120
PBE0	RECP	[24]+pol	[25]	1.995	2.443	2.586	2.804	118.0	120	120	120
PBE+U	AE DKH	LCGTO+FF+DF	[5]	1.972	–	–	–	117.7	–	–	–
PBE0	RECP	[24]+pol	[25]	1.983	2.429	2.571	2.790	119.0	120	120	120
PBE0	RECP	[27]	[28]	1.977	2.419	2.566	2.785	119.3	120	120	120
CCSD(T)	RECP	(TZ2D)	[22]	1.974	2.413.	–	–	120	120	–	–
CCSD(T)	RECP/LPP		[23]	1.982				120	–	–	–
CASPT2	DKH	ANO-RCC	[4]	1.961	–	–	–	120	–	–	–
MP4	RECP	[24]+d	[29]	1.976	2.379	2.536	2.749	–	–	–	–
MP2	RECP	(TZ2D)	[22]	1.966	2.397	–	–	–	–	–	–
Rec.			[30]	1.943	2.373	2.516	2.733	116.0	120	120	120
Exp. (e-values)			[31]	–	2.374(10)	2.516(8)	2.735(6)	–	114.5(24)	117.2(17)	116.6(10)
Exp. (g-values)			[31, 32]	1.968(10)	2.417(6)	2.557(4)	2.768(3)	–	111.5(20)	115.0(11)	115.6(6)
Exp. (g-values)			[33, 34]	–	2.403(5)	2.553(5)	–	–	117.9(1.3)	115.3(10)	–

pw:present work. ^{RECP}:Relativistic effective core potential; P:[35] note the value is erroneously given in [3]; Exp.(e-values) and Exp.(g-values): Equilibrium and thermally averaged values respectively;

di-augmented with diffuse function on X-atoms; AE: All electron are correlated in MP2 calculation; DKH: Douglas-Kroll-Hess; RCC:Relativistic (semi-)core correction; pol: Diffuse function was added by the

authors to the basis set of ref.[24]; LPP+CPP: 5f-in-core large core pseudopotential (LPP), see [23]. Rec: Recommended values by the authors of ref [30].

Table II. Geometric parameters of lawrencium trihalides LrX_3

Method	Hamiltonian	Basis	Ref	Lr-X bond length (in Å)				X-Lr-X bond angle (in °)			
				LrF ₃	LrCl ₃	LrBr ₃	LrI ₃	LrF ₃	LrCl ₃	LrBr ₃	LrI ₃
HF	DC	cc-pVTZ	pw	2.024	2.474	2.624	2.850	117	120	120	120
HF	RECP/LPP		[23, 36]	2.037	—	—	—	120	—	—	—
B3LYP	DC	cc-pVTZ	pw	2.013	2.443	2.597	2.815	110.6	116.6	120	120
PBE	DC	cc-pVTZ	pw	2.010	2.428	2.583	2.80	109	114.5	120	120
CCSD(T)	RECP/LPP		[23]	2.020	—	—	—	114.9	—	—	—

LPP = 5f-in-core large core pseudopotential (LPP), see [23].

Table III. Summary of PBE calculations on LuF_3 with a fictitious hole of δ electrons. The total electronic energy is $-14880 + \Delta E$ E_h . Total charge $Q(\text{Lu})$ on the lutetium atom as well as valence orbital populations, including $4f$ occupation $4f^{open}$ of the open shell, from projection analysis are also given.

$14-\delta$	$\Delta E(E_h)$	$Q(\text{Lu})$	$4f$	$4f^{open}$	$5p$	$5d$	$6s$
13.80	-0.750	+1.73	13.80	13.0	6.00	1.1	0.1
13.85	-0.773	+1.69	13.86	12.3	6.00	1.1	0.1
13.90	-0.795	+1.65	13.91	10.8	6.00	1.1	0.1
13.95	-0.815	+1.62	13.95	9.4	6.00	1.1	0.1
13.98	-0.826	+1.61	13.97	8.9	6.00	1.1	0.1
14.00	-0.833						

Table IV. Populations of the orbitals ns , $(n-1)d$ and $(n-2)f$ for Lutetium ($n=6$) and Lawrencium ($n=7$) atoms in the trihalides molecules LuX_3 and LrX_3 ($X=\text{F}, \text{Cl}, \text{Br}, \text{I}$) using HF, B3LYP- and PBE-functionals and cc-pVDZ basis set. LuF_3 , LuCl_3 and LrF_3 , LrCl_3 are calculated in C_s -symmetry whereas LuBr_3 , LuI_3 and LrBr_3 , LrI_3 in C_{2v} -symmetry.

Method	Orbital	LuX_3				LrX_3			
		LuF_3	LuCl_3	LuBr_3	LuI_3	LrF_3	LrCl_3	LrBr_3	LrI_3
HF	$(n-2)f$	14.00	14.0	14.0	14.0	13.99	14.0	14.0	14.0
	$(n-1)d$	0.71	0.87	0.91	0.94	0.68	0.87	0.92	0.97
	ns	0.08	0.19	0.25	0.35	0.11	0.26	0.33	0.44
B3LYP	$(n-2)f$	13.99	14.0	14.0	14.0	13.98	13.99	14.0	14.0
	$(n-1)d$	0.97	1.18	1.25	1.32	0.91	1.11	1.17	1.26
	ns	0.11	0.25	0.32	0.43	0.20	0.35	0.43	0.56
PBE	$(n-2)f$	13.98	13.99	14.0	14.0	13.98	13.99	13.99	14.0
	$(n-1)d$	1.09	1.27	1.33	1.40	1.02	1.21	1.25	1.33
	ns	0.13	0.26	0.33	0.44	0.23	0.38	0.46	0.58

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